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Trolier-McKinstry, Susan
Shrout, Thomas, R.

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Office of Sponsored Programs
110 Technology Center Building
University Park PA 16802-7000

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9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
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800 North Quincy Street
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14. ABSTRACT
Piezoelectric single crystals in the lead ytterbium niobate-lead titanate and BiScO3-PbTiO3 systems were grown and characterized as high temperature piezoelectrics. The properties were quite good, with d33 coefficients as high as 2500 pm/V in PY N-PT. Epitoxial and fiber textured thin films were prepared by pulsed-laser deposition and chemical solution deposition, respectively. These films show the highest reported e31,f coefficients for high Tc films. In addition, it was determined that the amplitude dependence of the dielectric and piezoelectric response of the films can be described using a frequency-dependent Rayleigh approach.

15. SUBJECT TERMS
piezoelectric, single crystals, thin films

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Contract Information

Contract Number	N00014-01-1-0895
Title of Research	Crystal Growth and Thin Film Deposition of High Performance Piezoelectrics
Principal Investigator	T. R. Shrout and S. Trolier-McKinstry
Organization	Penn State

Technical Objectives

The objective of the program was the growth and characterization of high transition temperature (T_c) single crystal perovskites in both bulk and thin film form. Specifically, the $Pb(Yb_{1/2}Nb_{1/2})O_3$–$PbTiO_3$ (PYN-PT) and $BiScO_3$–$PbTiO_3$ (BS-PT) were targeted. These materials offer significantly higher transition temperature (T_c) and thus working temperature ranges, as compared to PMN-PT and PZN-PT Relaxor-based compositions.

Specific objectives for the program were the following:

- Growth of PYN-PT and BS-PT using high temperature flux method.
- Dielectric and piezoelectric characterization of single crystals, including capacitance vs. temperature and d_{33} from direct strain measurement.
- Electromechanical characterization using IEEE resonance.
- Growth of (001) PYN-PT and BS-PT thin films by sol-gel and pulsed laser deposition methods.
- Dielectric and electromechanical characterization of films

Technical Approach

Crystal growth parameters were arrived at based on differential thermal analysis (DTA) carried out on polycrystalline sample on the PYN-PT and BS-PT systems. Using a DSC 2920 Differential Scanning Calorimeter from 30 to 1350°C, the thermal hysteresis between melting crystallization points was determined. From these results, stoichiometric mixtures of the desired composition(s) were mixed

with various amounts of flux (Pb_3O_4 and/or Bi_2O_3) and loaded into platinum (PT) crucibles. Growth was carried out in a high temperature furnace with automated temperature control. A typical run was a soak temperature at 1200°C, followed by cooling to ~ 900°C and subsequent furnace cooling to room temperature. Figure (1) shows optical photograph of PYN-PT rhombohedral crystal.

From crystals 3–5 mm in size, samples for dielectric and piezoelectric properties were first oriented using real-time Laue and polished into flat and parallel surface onto which electrodes were sputtered. High temperature dielectric behavior was determined using a multi-frequency LCR meter (HP 4289G) with a computer-controlled temperature chamber. High field measurements included polarization and strain hysteresis using a modified Sawyer-Tower circuit and linear variable differential transducer (LVDT). The piezoelectric coefficient d_{33} was calculated from the slope of strain versus field curves. Electromechanical coupling coefficients were determined on longitudinal and lateral mode bars and plates, as specified by IEEE standards.

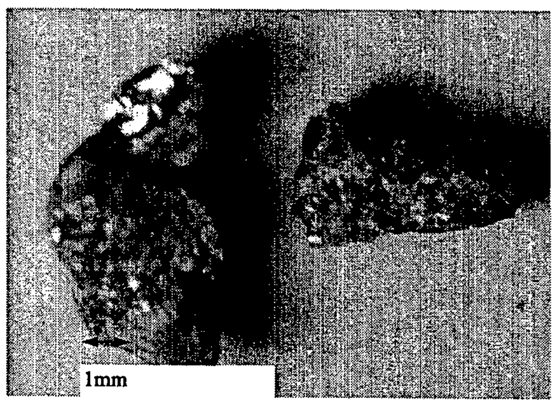


Figure 1. Optical photograph of PYN-xPT rhombohedral single crystals.

Thin films have been grown both by pulsed laser deposition (PLD) and by sol-gel methods. (001) orientation was achieved in PLD films was achieved by growing epitaxial films on $SrRuO_3/LaAlO_3$ or $SrRuO_3/SrTiO_3$ substrates. Orientation control is being approached in sol-gel films on Pt/coated Si (where no epitaxial match is available) by control of nucleation. Dielectric and piezoelectric properties have been measured using low frequency LCR meters (HP 4192) with a hot-plate for temperature control. High field measurements were made using a Radiant Technologies RT66A Ferroelectrics tester. $e_{31,f}$ coefficients were measured by the wafer flexure method.

Summary

Among the accomplishments on the program are:

- Crystal growth PYN-xPT in the compositional range of x=0.2 – 0.75PT as shown in Figure 2. Note the composition of the morphotropic phase boundary (~ x= 0.5).
- Confirmed the transition temperature behavior in the PYN-PT system, as shown in Figure 3.
- Confirmed high T_c of MPB coupled by T_c > 330°C, as originally observed for polycrystalline materials.
- Determined the dielectric and piezoelectric properties as a function of composition, noting the performance enhancement near MPB (see Fig 4).
- Contrasted the temperature stability of PYN-PT with PZN-PT, as seen in Figure 5.
- Crystal growth of BS-PT tetragonal crystals with Tc > 460°C, the highest (see Fig. 6).
- Demonstrated epitaxial film growth and crystal anisotropy in PYN-PT films (See Fig. 7).
- Demonstrated epitaxial film growth in BS-PT films (See Fig. 8).
- Demonstrated good piezoelectric properties ($e_{31,f}$= - 12C/m^2) in BS-PT films (See Fig. 9).
- Developed a sol-gel process for preparing PYN-PT films on platinum – coated Si (See Fig. 10).
- Demonstrated that sol-gel PYN-PT films on platinum – coated Si show the best (100) orientation when the heating rate during the crystallization is <20°C/sec.
- Demonstrated good piezoelectric properties in (100) sol-gel derived PYN-PT films on MgO ($e_{31,f}$ = -10.2 C/m^2) and Pt-coated Si (~-8 C/m^2)
- Demonstrated that PYbN-PT films show dielectric and piezoelectric nonlinearity can be described by Rayleigh approaches (See Fig. 11). (100) films show larger amounts of nonlinearity than do (111) oriented films.
- Determined conditions under which 180° domain walls can contribute to the piezoelectric response.

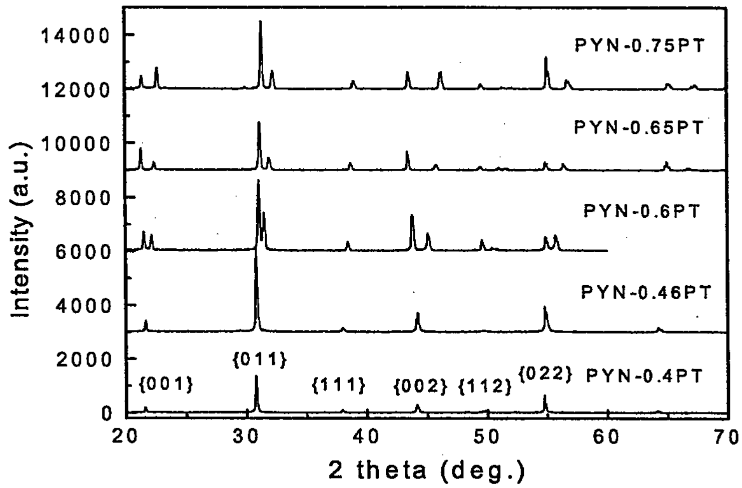


Figure 2. XRD of PYN-xPT single crystals in the range $0.4 \leq x \leq 0.75$ with 1 mol% Ba^{2+} additive.

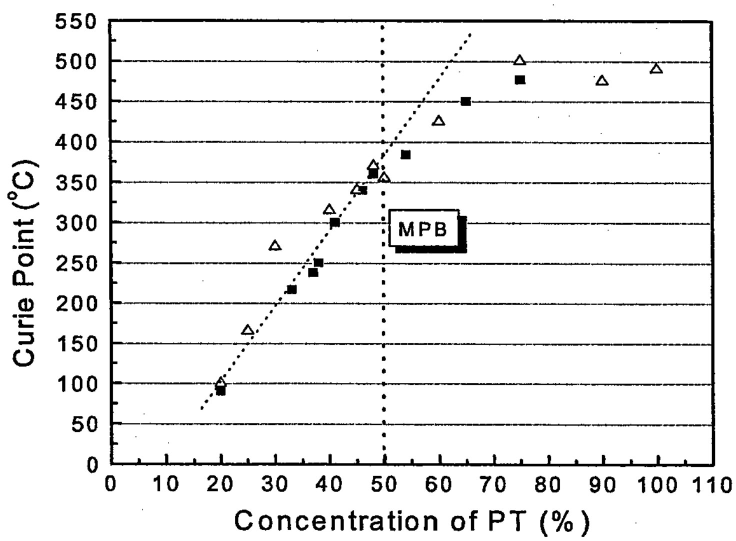


Figure 3. Curie temperature of PYN-xPT ($0.2 \leq x \leq 0.8$) single crystals measured at 10 kHz (Δ polycrystalline data).

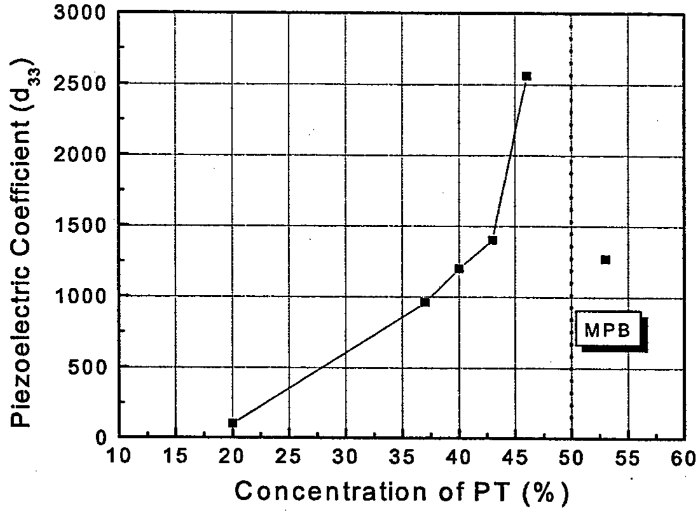


Figure 4. Piezoelectric coefficient of PYN-xPT $(0.2 \leq x \leq 0.8)$ single crystal series.

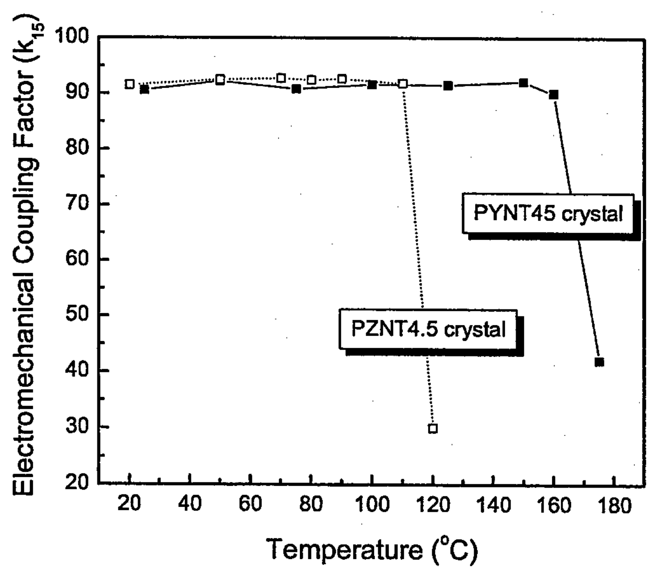


Figure 5. Electromechanical coupling factor k_{15} as a function of temperature for PYNT4 and PZNT4.5 crystals.

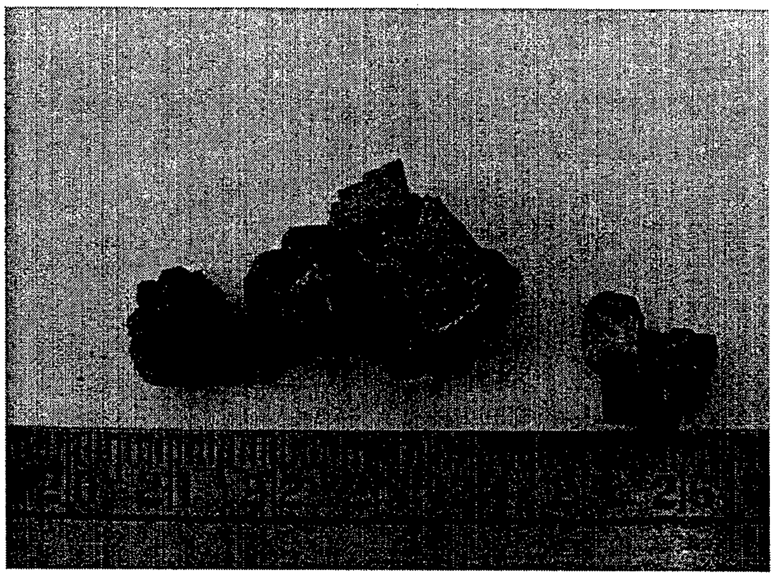


Figure 6(a). The photo of BSPT single crystals with rectangular shape.

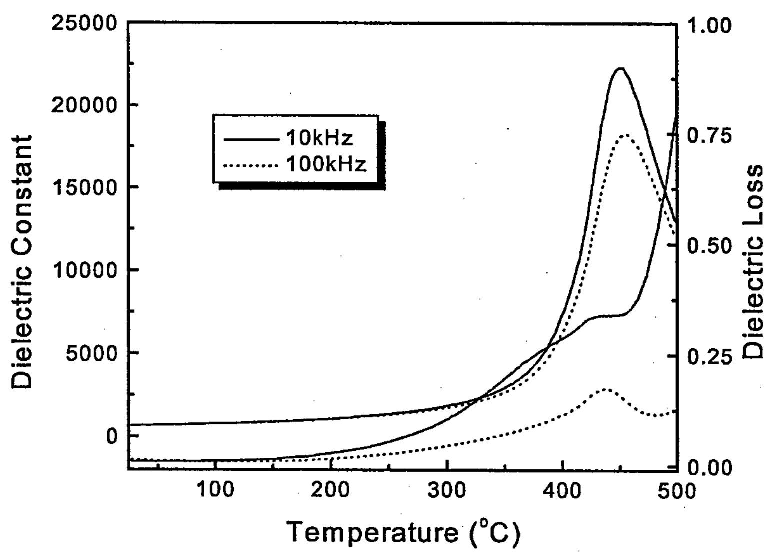
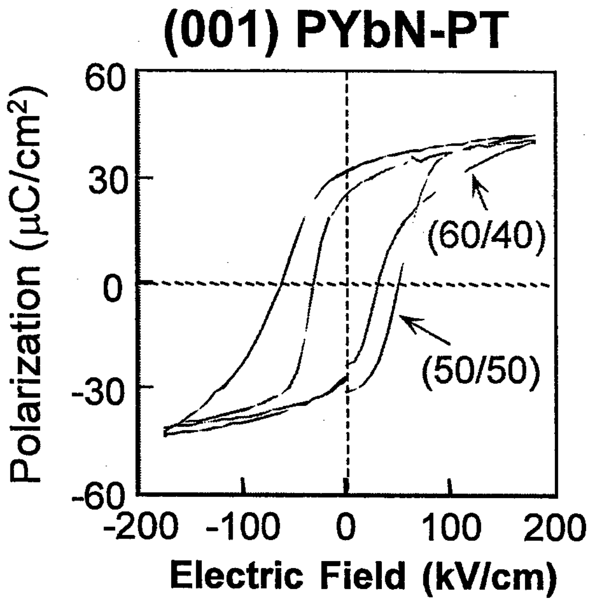
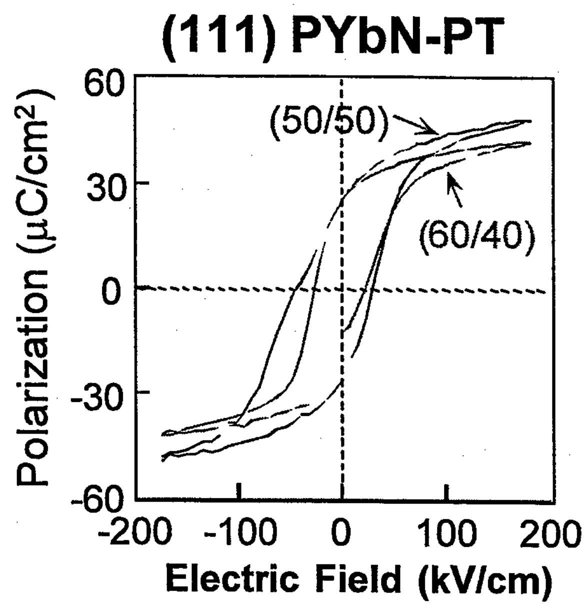


Figure 6(b). Dielectric constant and dielectric loss of BSPT66 single crystal as the function of temperature.



	(50/50)	(60/40)
P_r ($\mu C/cm^2$)	30	26
ε_r	1000	1000
$e_{31,f}$ (C/m^2)	**-12**	**-9**



	(50/50)	(60/40)
P_r ($\mu C/cm^2$)	25	24
ε_r	1300	1300
$e_{31,f}$ (C/m^2)	**-3.3**	**-2.5**

Fig. 7: Crystal anisotropy in PYN-PT films.

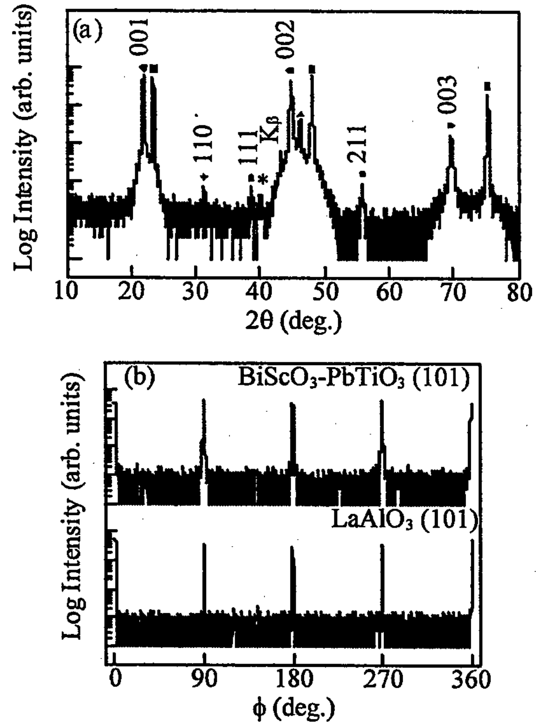


Fig. 8: X-ray diffraction pattern of epitaxial film growth in BS-PT50/50 film grown by pulsed laser deposition.

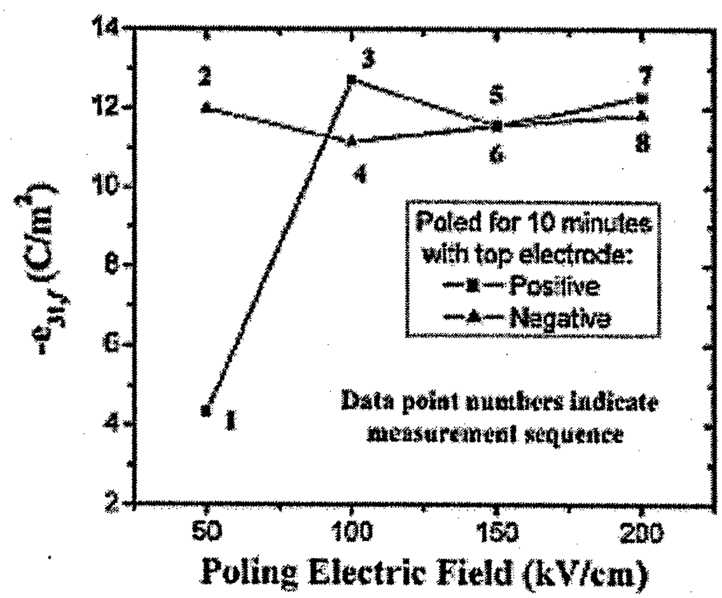


Fig. 9: Piezoelectric properties of BS-PT 40/60 films.

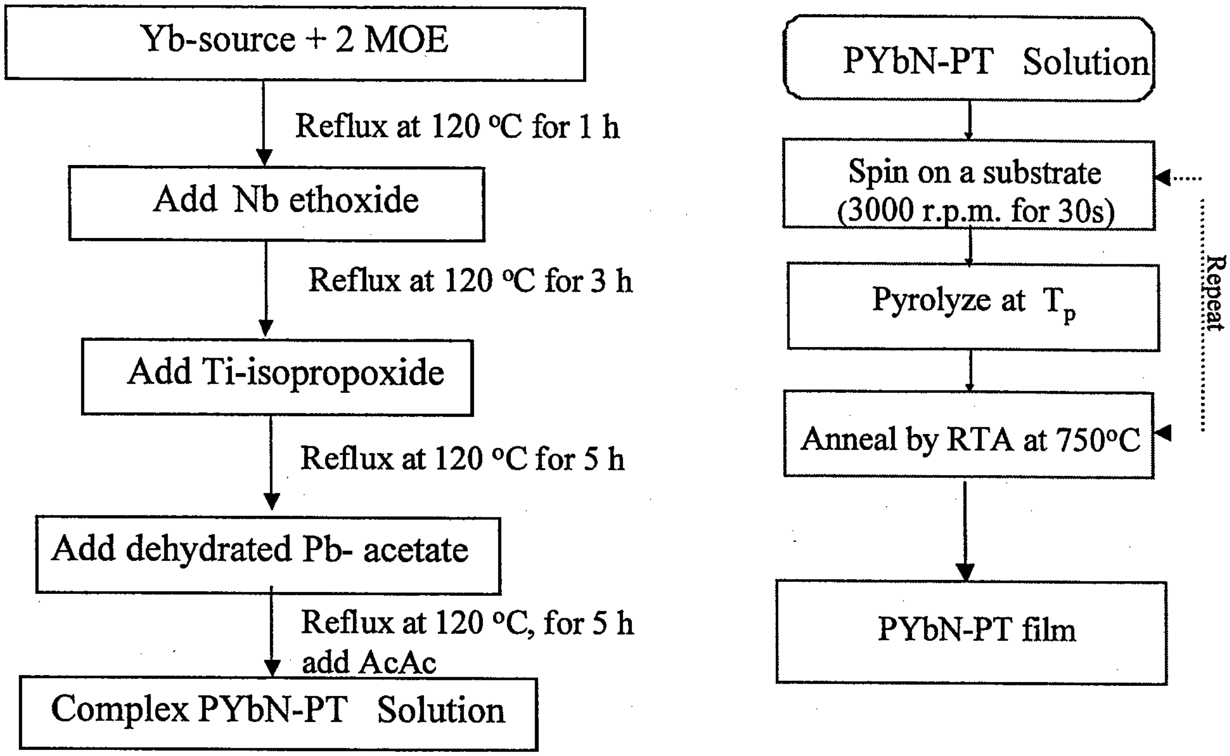


Fig. 10: Flow chart for sol-gel deposition of PYN-PT films

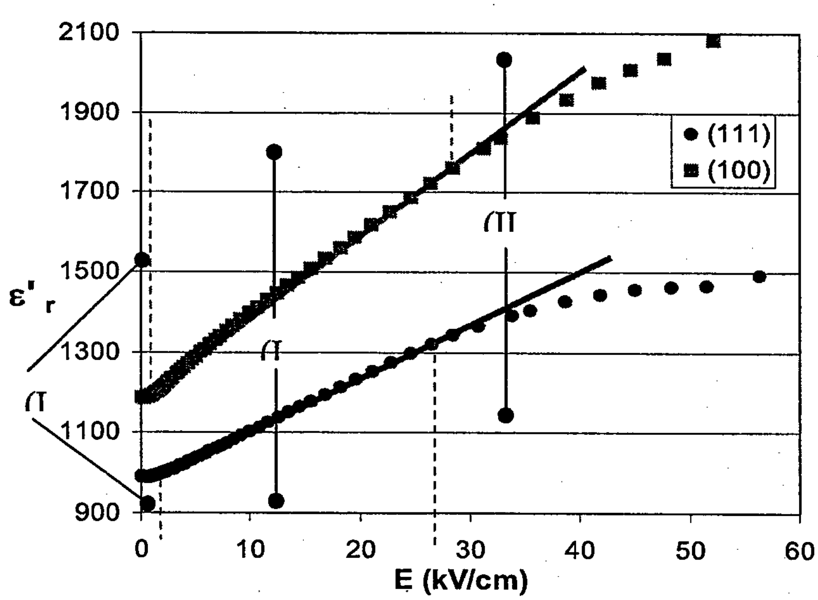


Fig. 11: Dielectric Nonlinearity in sol-gel PYbN-PT films

ONR Database Statistics

Papers published in refereed journals citing ONR support: 12

Books or chapters published citing ONR support: 2

Technical Reports & Non-refereed papers: 5

Patents granted citing ONR support: 0

Presentations: 26

Papers in press in refereed journals citing ONR support: 1

Books or chapters in press citing ONR support: 0

Invention disclosures citing ONR support: 0

Patents pending citing ONR support: 0

Degrees granted: 0 (Nazanin Bassiri Gharb is expected to defend her Ph.D. in May 2005).

PI-CoPI: 2 total, 1 woman

Post-docs: 2 total, 1 minority

Grad students: 1 woman

Publications

1. Shujun Zhang, Laurent Lebrun, Sorah Rhee, Richard E. Eitel, Clive A. Randall, and Thomas R. Shrout, "Crystal Growth and Characterization of New High Curie Temperature (1-x)$BiScO_3$-x$PbTiO_3$ Single Crystals," J. of Crystal Growth, 236, 210-216 (2002).
2. Shujun Zhang, Sorah Rhee, Clive A. Randall, and Thomas R. Shrout, "Dielectric and Piezoelectric Properties of High Curie Temperature Single Crystals in the $Pb(Yb_{1/2}Nb_{1/2})O_3$-x$PbTiO_3$ Solid Solution Series," Jpn. J. Appl. Phys., Vol. 41, 722–726 (2002).
3. Shujun Zhang, Paul W. Rehrig, Clive Randall, and Thomas R. Shrout, "Crystal Growth and Electrical Properties of $Pb(Yb_{1/2}Nb_{1/2})O_3$–$PbTiO_3$ Perovskite Single Crystals," J. of Crystal Growth, 234, 415–420 (2002).

4. Richard E. Eitel, Clive A. Randall, Thomas R. Shrout, Paul W. Rehrig, Wes Hackenberger, and Seung-Eek Park, "New High Temperature Morphotropic Phase Boundary Piezoelectric Based on Bi(Me)O_3–PbTiO_3 Ceramics," Jpn. J. Appl. Phys., Vol. 40, 5992-6002 (2001).

5. Richard E. Eitel, Clive A. Randall, Thomas R. Shrout, and Seung-Eek Park, "Preparation and Characterization of High Temperature Perovskite Ferroelectrics in the Solid Solution (1-x)$BiScO_3$–x$PbTiO_3$," Jpn. J. Appl. Phys., Vol. 41, 1–6 (2002).

6. Shujun Zhang, Shashank Priya, Eugene Furman, Thomas R. Shrout, and Clive A. Randall, "A Random-field Model for Polarization Reversal on $Pb(Yb_{1/2}Nb_{1/2})O_3$–$PbTiO_3$ Single Crystals," J. Appl. Phys. 91, 6, p. 6002 (2002).

7. Shujun Zhang, Laurent Lebrun, Sorah Rhee, Clive A. Randall, and Thomas R. Shrout, "Shear-mode Piezoelectric Properties of $Pb(Yb_{1/2}Nb_{1/2})O_3$–$PbTiO_3$ Single Crystals," Appl. Phys. Lett., 81, 5, p. 892 (2002).

8. T. Yoshimura and S. Trolier-McKinstry, "Transverse Piezoelectric Properties of Epitaxial $Pb(Yb_{1/2}Nb_{1/2})O_3$-$PbTiO_3$ (50/50) Films," J. Cryst. Growth 229 445-449 (2001).

9. T. Yoshimura and S. Trolier-McKinstry, "Phase Development and Electrical Properties of $Pb(Yb_{1/2}Nb_{1/2})O_3$-$PbTiO_3$ Epitaxial Films," Integr. Ferroelectr. 50, 33-42 (2002).

10. T. Yoshimura and S. Trolier-McKinstry, "Growth and Piezoelectric Properties of $Pb(Yb_{1/2}Nb_{1/2})O_3$-$PbTiO_3$ Epitaxial Films," J Appl. Phys. 92 (7): 3979-3984 (2002).

11. T. Yoshimura and S. Trolier-McKinstry, "Growth and Properties of (001)$BiScO_3$-$PbTiO_3$ Epitaxial Film," Appl. Phys. Lett. 81 (11): 2065-2066 (2002).

12. J. C. Nino and S. Trolier-McKinstry, "Dielectric, Ferroelectric, and Piezoelectric Properties of (001) $BiScO_3$–$PbTiO_3$ Epitaxial Films Near the Morphotropic Phase Boundary," J. Mat. Res. 19 (2) 568 – 572 (2004).

Books and Chapters

1. Chapter 1. High Performance, High Temperature Perovskite Piezoelectric Ceramics, Piezoelectric Materials for the User: Reviews on Standard and Emerging Materials and Technologies, Their Properties, and Their Applications. Editor N. Setter
2. Piezoelectric Single Crystals and Their Application, edited by S. Trolier-McKinstry, L.E. Cross, and Y. Yamashita, published by S. Trolier-McKinstry (2004). (and chapters therein)

Technical Reports

1. "The Study of Fatigue Anisotropy in $Pb(Zn_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ Ferroelectric Single Crystals," M. Ozgul, K. Takemura, S. Trolier-McKinstry, and C.A. Randall, 10th US-Japan Seminar on Dielectric and Piezoelectric Ceramics, September 2001, Providence, R.I.
2. "New High-Temperature Morphotropic Phase Boundary Piezoelectrics Based on $Bi(Me)O_5$-$PbTiO_3$ Ceramics," R. Eitel, C.A. Randall, T.R. Shrout, P. Rehrig, Wesley Hackenberger, and S. Park, 10th US-Japan Seminar on Dielectric and Piezoelectric Ceramics, September 2001, Providence, R.I.
3. T. Yoshimura and S. Trolier-McKinstry, "Piezoelectric Properties of $Pb(Yb_{1/2}Nb_{1/2})O_3$ – $PbTiO_3$ Epitaxial Films with (100) and (111) Orientation," poster presentation at the US-Japan Meeting on Dielectric and Piezoelectric Ceramics, Sept. 26 – 29, 2001, Providence, RI
4. N. Bassiri Gharb and S. Trolier-McKinstry, "Dielectric Nonlinearity in (100) PYbN-PT Thin Films," Proceedings International Symposium on Applications of Ferroelectrics, 2004.
5. Shujun Zhang, Laurent Lebrun, Sorah Rhee, Clive A. Randall, and Thomas R. Shrout, "Dielectric and Piezoelectric Properties as a Function of Temperature for $Pb(Yb_{1/2}Nb_{1/2})O_3$-$PbTiO_3$ Single Crystals," Proceedings of the 13th IEEE

International Symposium on Applications of Ferroelectrics, edited by Grady White and Takaaki Tsurumi, Piscataway, NJ, 2002, p. 455

Articles in Press

1. N. Bassiri Gharb and S. Trolier-McKinstry, "Dielectric Nonlinearity of $Pb(Yb_{1/2}Nb_{1/2})O_3$-$PbTiO_3$ Thin Films with {100} and (111) Crystallographic Orientation," accepted by the Journal of Applied Physics

Honors/Awards/Prizes

- IEEE UFFC Outstanding Paper of the Year Award for 2000: T.A. Ritter, X. Geng, K.K. Shung, P.D. Lopath, S. Park, and T.R. Shrout, "Single Crystal PZN/PT-Polymer Composites for Ultrasound Transducer Applications," IEEE Trans. UFFC, Vol. 47, No. 4, July 2000.
- Susan Trolier-McKinstry. promoted to full professor, July 2002
- Susan Trolier-McKinstry, fellow of the American Ceramic Society, 2004.
- Nazanin Bassiri Gharb, graduate student poster award winner, International Symposium on Applications of Ferroelectrics, 2004.